

Electrochemical in-situ reaction cell for X-ray scattering, diffraction and spectroscopy

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Abstract

An electrochemical in-situ reaction cell for hard X-ray experiments with battery electrodes is described. Applications include the small angle scattering, diffraction, and near-edge spectroscopy of lithium manganese oxide electrodes.

Key words: lithium battery; electrochemistry; small angle scattering; spectroscopy; in-situ cells.

1 Introduction

On-line monitoring of changes in materials under chemical reactions is usually performed by using in-situ reaction chambers. In recent years, numerous X-ray in-situ chambers have been designed for battery research applications. Since some of the battery electrode materials are very sensitive to corrosion under ambient atmosphere, this includes in particular the alkaline metal based systems, such as lithium batteries, the sealing of the cells plays a very important role.

While many different cell designs have been successfully developed and tested for short term experiments, to the best of our knowledge, no cell has been reported yet which allows for experiments that extend over several days or even weeks. Charging and discharging reactions in batteries are pronouncedly limited by diffusion and may take hours. As the structure of electrodes may be altered by the number of charge and discharge cycles, experiments often take as long as weeks or months.

When exposed to ambient atmosphere, the lithium most likely reacts with the nitrogen in air to lithium nitride or, with according humidity, to lithium hydroxide. Also, some of the electrolytes used in batteries may form very aggressive compounds, for instance LiPF_6 , which forms hydrofluoric acid when in contact with ambient humidity.

Those corrosive reactions are immanent to batteries and have to be minimized by using a proper sealing. Regular battery test cells, which are not used for in-situ

studies, are usually very massive and satisfy the strict sealing requirements and allow cycling experiments for several months.

In contrast, in-situ cells need X-ray windows and thus are more sensitive to leakage. In some of them, leakage problems are overcome by extensive use of sealants, and those cells are often for the one-time use only.

Here we present a massive and handy re-usable cell with Beryllium X-ray windows and O-rings for sealing. It allows charging and discharging of the battery assembly even for several days without noticeable traces of corrosion in the electrodes.

The cell design was meant to allow the cell to be employed in the transmission mode at any hard X-ray source. In particular, the cell was tested at beamline 12-ID [1] at BESSRC-CAT, Advanced Photon Source, Argonne/IL, and at beamlines 2-1 and 2-3 at Stanford Synchrotron Radiation Laboratory, Menlo Park/CA.

2 Design of the in-situ cell

Figure 1 displays a schematic sketch of the flat and cylindric cell. The main support of the cell is a stainless steel disk (12 cm diameter) and a disk from polypropylene (PP, 9 cm diameter), both of 5 mm thickness. With steel bolts (size M 5), both disks are pressed together and then may contain the electrode sample, an ion-conducting separator, the electrolyte and a counter electrode. Sealing of the cell is necessary to prevent the electrolyte from drying out or to prevent the sample from chemical

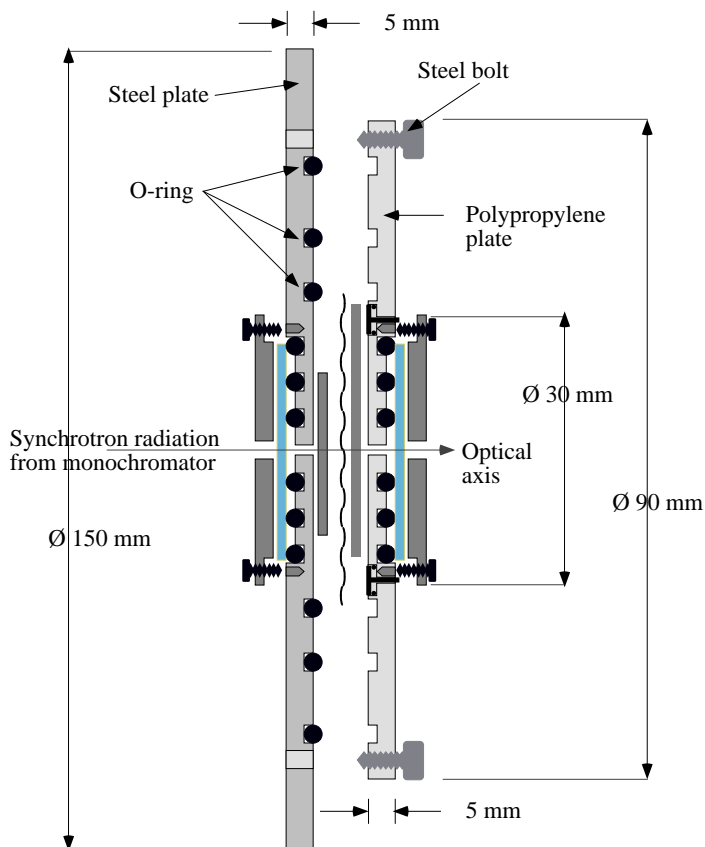


Fig. 1. Cross section overview of in-situ cell. Note that not all of the parts refer to the same scale.

reactions with the ambient atmosphere.

The interface between steel disk and PP disk can be considered as the sample compartment, which is sealed by three concentric BUNA O-rings which have different diameters. According grooves are provided in both disks.

Figure 2 displays a magnification of the cell part that contains the electrode assembly. Both disks have a hole of $1 \text{ mm} \times 2.5 \text{ mm}$ in their center to allow the X-ray beam to pass through the cell. The holes on either side of the cell are capped with a Beryllium disk of 380 micrometer thickness. The contact between the Beryllium disks and the steel disk and the PP disk, respectively, is also sealed with three small

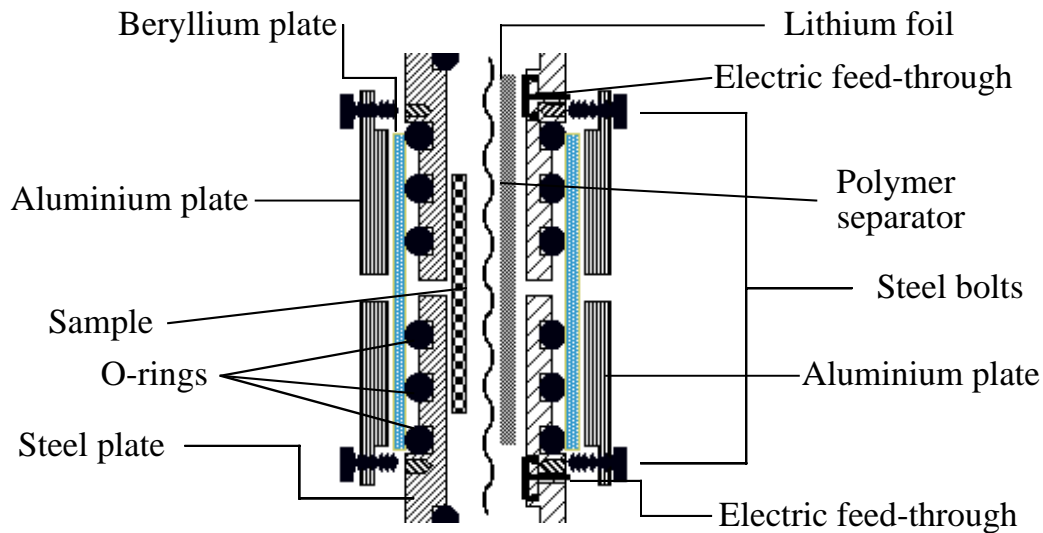


Fig. 2. Magnified cross section of the central cell parts.

concentric BUNA O-rings. On either side, an aluminium disk with 30 mm diameter serves to fix and press the Beryllium disks on either cell plate. In their center, the aluminium disks have an opening with 7 mm diameter to allow for the X-ray beam to pass through. The thickness of disks and the width of holes determines



Fig. 3. Photograph of the in-situ cell, showing PP disk on top of stainless steel disk. The ruler shows length scale in inches.

the aspect ratio which is necessary to cover a desired Q-range for wide-angle X-ray diffraction. In the present case, a maximum 2Θ -angle of about 45° was given

which allowed to resolve the [111] Bragg reflex of LiMn_2O_4 at X-ray energies of around 6500 eV. Of course, by choosing higher energies, the entire diffractogram becomes *compressed* and will be resolved in the 2Θ -angle of about 45° , however, on the cost of spatial resolution.

The Be foils are coated with 25 micron thick sticky Kapton tape to prevent contact with the corrosive electrolyte.

The working electrode is in direct contact with the stainless steel plate which allows for direct electric contacting. The PP plate has two feed-throughs with stainless steel bolts which serve as contacts to the lithium counter electrode and an optional reference electrode. Each of the two steel bolts is sealed with a tiny O-ring of 2 mm diameter; these inlets are the weakest cell parts in terms of contamination from ambient atmosphere. After several days of operation, that side of the lithium foil which is next to the steel bolts, exhibits traces of typical black lithium nitride - an indication that nitrogen has diffused around the O-ring. Since this effect was confined to an uncritical area in the cell, we did not attempt to improve the sealing.

Figure 3 shows the assembled cell with the PP plate on top of the stainless steel plate. Two metal strips are contacted with the bolts in the feed-through for reference and counter electrodes. Numerous drilled holes in the metal plate allow for a versatile mounting of the cell at the beamlines.

At SSRL and at APS, we assembled and sealed the cell in a portable helium filled glove bag on site in their chemistry labs. Also, during one beam time, we assembled

the cell in our home lab at LBNL and brought it to SSRL for experiments.

To enhance the sealing safety of the cell during experiments, we wrapped it in a conventional ziplock bag, filled with helium. It turned out, however, that the cell will remain fine without significant contamination or corrosion for more than four days without keeping it in helium.

3 First experimental results

First experimental results were obtained with a lithium battery in the cell. Lithium manganese oxide, cast as a porous electrode (40 micron thickness) on thin aluminium foil (25 micron), with a polymer separator, electrolyte, and with lithium foil (125 micron) as counter electrode, was assembled to a battery cell [1].

X-ray absorption near edge spectra were obtained at SSRL, BL 2-1, during deep discharge of the battery cell, where the manganese is being reduced from an average manganese oxidation state of 3.5 towards 2.0 by inserting lithium into the spinel host lattice. This is shown for 3 different states of charge in Figure 4. At the same beamline, X-ray diffractograms were recorded during the discharging. Figure 5 displays the [111] Bragg reflex of the $\text{Li}_{1+x}\text{Mn}_2\text{O}_4$ spinel lattice for two different X-ray energies at Q-values of about 1.85 and 1.9 \AA^{-1} , respectively. After discharging, this reflects split up into two peaks at Q-values of about 1.37 and 1.39 \AA^{-1} . This cubic \rightarrow tetragonal phase transition is known as the Verwey transition and caused by the Jahn-Teller effect. The shift of the [111] peak with drawn line (6500

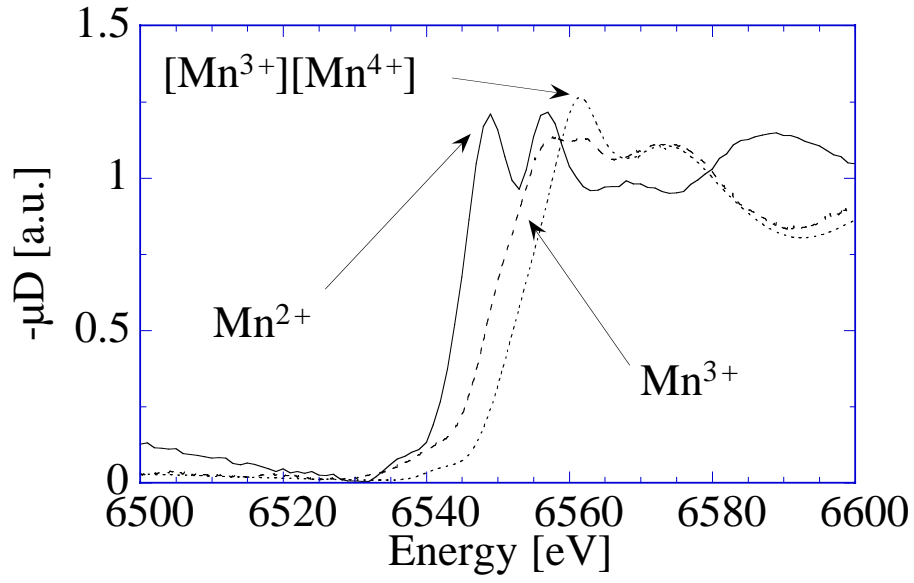


Fig. 4. XANES spectra of $\text{Li}_{1+x}\text{Mn}_2\text{O}_4$ for three different oxidation stages of Mn.

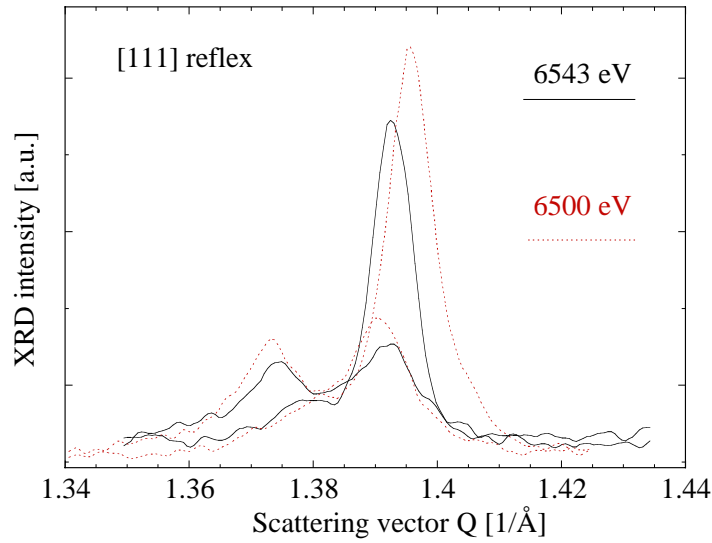


Fig. 5. [111] Bragg reflex in the uncharged (single peak) and deeply discharged (splitted peak) state for energies at 6543 eV (solid) and 6500 eV (dotted).

eV photon energy) towards lower Q and its lower intensity is not due to anomalous scattering of manganese atoms, but due to different states of charge in the electrode.

EXAFS spectra were recorded at beamline 2.3 at SSRL. The evolution of their according Fourier amplitude during the entire discharge process is displayed in Figure 6. While the Mn-O distance remains constant during lithiation ($R = 1.9 \text{ \AA}$), the Mn-Mn distance ($R = 2.8 \text{ \AA}$) experiences a split ($R = 2.65 \text{ \AA}$ and $R = 3.1 \text{ \AA}$) similar to the split observed in XRD.

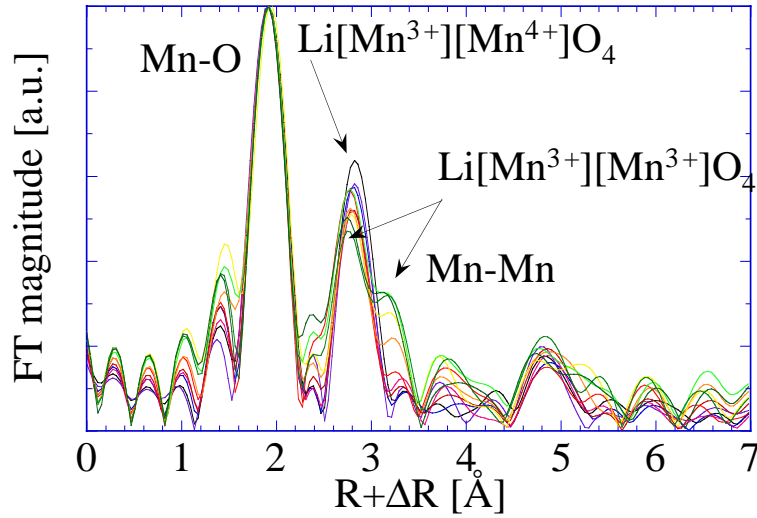


Fig. 6. Evolution of EXAFS fourier magnitude for Mn during discharging from average Mn valence 3.5 to 3.

Anomalous small angle X-ray scattering (ASAXS) was carried out at the Advanced Photon Source (APS, BESSRC-CAT) for a period of 40 hours, during which the battery was gently charged. Scattering curves were recorded at 20 different X-ray energies around 6530 eV near the manganese (Mn) K-shell absorption edge to allow for contrast variation due to anomalous scattering of the Mn. Results are shown in

Figure 7.

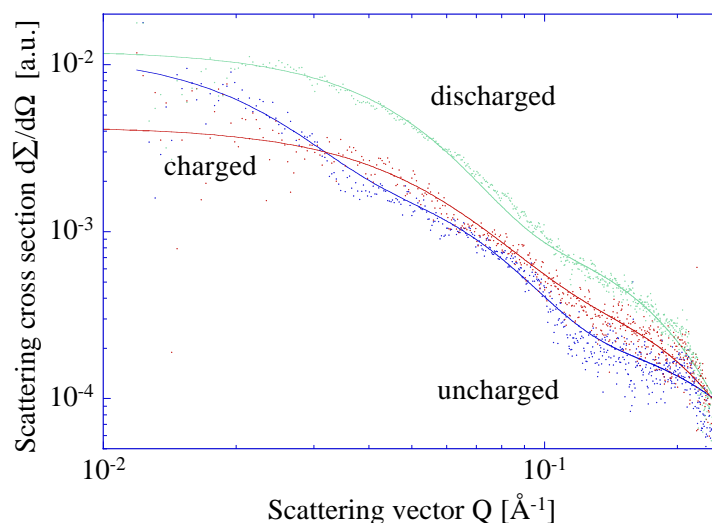


Fig. 7. Scattering curves of manganese oxide in electrode matrix for three different states of charge.

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